VIII. SUMMARY AND DISCUSSION OF RESULTS.

Backer and co-workers have studied the influence, which a symmetrical, compact and spherical shape of a molecule (a ,,filled" molecule) exerts on its properties, in particular on the M.P., the crystal system and the solubility. For this purpose ,,radiate" compounds were prepared consisting of a central atom with four equal groups linked to it. Compounds of the following types have been prepared:

$C(SR)_4$, $Si(SR)_4$, $Ge(SR)_4$, $Sn(SR)_4$,
$C(CH_2OR)_4$, $C(CH_2SH)_4$, $C(CH_2SO_3H)_4$, $C(CH_2SR)_4$, $C(CH_2SOR)_4$
$C(CH_2SO_2R)_4$, $C(CH_2CO_2R)_4$

The alterations in the properties which were caused bij changes in R, have been studied and the following rules have been found.

When the groups R are straight chains of hydrocarbons of various length, then the M.P. is lowered by elongating the chains, although the molecular weight is raised. At a certain point however, the influence of the greater molecular weight predominates and the M.P.'s gradually begin to raise. When the groups R are isomeric hydrocarbon rests with an equal number of C atoms, the most ramified compound will have the highest M.P. and in general the lowest solubility. It is often much more difficult to prepare these highly branched compounds than the compounds with straight side chains, owing to steric hindrance, which is also responsible for the failure of some reactions that generally succeed with the latter substances. The crystalline system often shows tetragonal symmetry.

Later it was shown that derivatives of hexamethylbenzene, consisting of a benzene nucleus with 6 equal substituents, ,,plano-radiate" compounds, obey the same rules:

$C_6(CH_2Br)_6$, $C_6(CH_2OR)_6$, $C_6(CH_2SH)_6$,
$C_6(CH_2SR)_6$, $C_6(CH_2SO_2R)_6$, $C_6(CH_2SO_3H)_6$.

Their crystals show preference for trigonal or pseudo-trigonal symmetry. It was therefore interesting to complete this investigation with a series of benzene derivatives, with substituents linked directly to the nucleus.

Compounds of the types $C_6(OAc)_6$ and $C_6(NHAc)_6$ were

chosen. For the preparation of the necessary *hexahydroxybenzene* the method of Nietzki and Benckiser was followed, as the preparation according to Homolka's patent gave a poor yield (see reaction scheme page 9).

The *hexa-aminobenzene* was prepared after Flürscheim and Holmes by reducing trinitrotriaminobenzene with phenylhydrazine. This substance could easily be made by the interaction of alcoholic ammonia and trichlorotrinitrobenzene, the reaction scheme being aniline - trichloro-aniline - trichlorobenzene - trinitrotrichlorobenzene - trinitrotriaminobenzene, instead of F. and H's scheme: trinitrotoluene - trinitrobenzoic acid - trinitrobenzene - dinitroaniline - pentanitro-aniline - trinitrotriaminobenzene.

The following compounds were prepared:

Hexavalent esters of hexahydroxybenzene.		M.P.
Acetate	$C_6(O_2CCH_3)_6$	222° (dec.)
Propionate	$C_6(O_2CCH_2CH_3)_6$	137°
n.Butyrate	$C_6\{O_2C(CH_2)_2CH_3\}_6$	135°
Isobutyrate	$C_6\{O_2CCH(CH_3)_2\}_6$	157°
Valerate	$C_6\{O_2C(CH_2)_3CH_3\}_6$	109°
Isovalerate	$C_6\{O_2CCH_2CH(CH_3)_2\}_6$	167.5°
Methylethylacetate	$C_6\{O_2CCH(CH_3)(C_2H_5)\}_6$	115.5°
Trimethylacetate	$C_6\{O_2CC(CH_3)_3\}_6$	316° (dec.)
Heptanoate	$C_6\{O_2C(CH_2)_5CH_3\}_6$	85.5°
Hendecanoate	$C_6\{O_2C(CH_2)_9CH_3\}_6$	89.5°
Phenylacetate	$C_6(O_2CCH_2C_6H_5)_6$	185.5°
Benzoate	$C_6(O_2CC_6H_5)_6$	313° (dec.)
p.Methylbenzoate	$C_6(O_2CC_6H_4CH_3)_6$	333° ,,
p.Chlorobenzoate	$C_6(O_2CC_6H_4Cl)_6$	328° ,,
and the pentavalent ester of trimethylacetic acid	$C_6OH\{O_2CC(CH_3)_3\}_5$	180.5°

Hexa-acylderivatives of hexa-aminobenzene.		Decomp. point
Acetyl	$C_6(NHCOCH_3)_6$	358°
Propionyl	$C_6(NHCOCH_2CH_3)_6$	360°
n.Butyroyl	$C_6\{NHCO(CH_2)_2CH_3\}_6$	360°
Isobutyroyl	$C_6\{NHCOCH(CH_3)_2\}_6$	384°

n.Valeroyl	$C_6\{NHCO(CH_2)_3CH_3\}_6$	335°
Isovaleroyl	$C_6\{NHCOCH_2CH(CH_3)_2\}_6$	366°
Methylethylacetyl	$C_6\{NHCOCH(CH_3)(C_2H_5)\}_6$	345°
Trimethylacetyl	$C_6\{NHCOC(CH_3)_3\}_6$	367°
Heptanoyl	$C_6\{NHCO(CH_2)_5CH_3\}_6$	329°
Phenylacetyl	$C_6(NHCOCH_2C_6H_5)_6$	340°
Benzoyl	$C_6(NHCOC_6H_5)_6$	405°
p.Methylbenzoyl	$C_6(NHCOC_6H_4CH_3)_6$	above 400°
p.Chlorobenzoyl	$C_6(NHCOC_6H_4Cl)_6$	,, ,,

Only the acetic derivatives were known.

The compounds with aliphatic acids were prepared by heating hexahydroxybenzene and hexa-aminobenzene with the anhydrides (the anhydride of hendecanoic acid, m.p. 35°, was prepared for the first time), those with aromatic acids by means of the chlorides of the corresponding acids. The yields were good with hexahydroxybenzene, much lower with hexa-aminobenzene. Some derivatives of this substance could not be obtained at all with acid anhydrides; it was necessary to use the acid chloride and pyridine method. The melting points (decomposition points) are high.

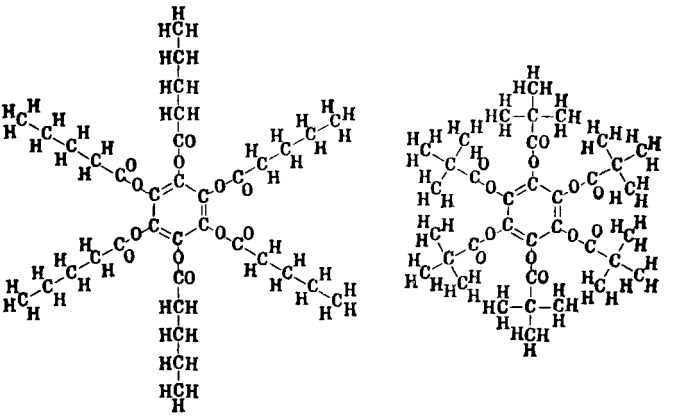
The *esters of hexahydroxybenzene* show very clearly the decrease in M.P., when the side chains become longer. When the chain reaches a length of ten C atoms, however, the M.P. is raised a little.

$C_6(O_2CCH_3)_6$	M.P. 222° (decomp.)
$C_6(O_2CCH_2CH_3)_6$	137°
$C_6\{O_2C(CH_2)_2CH_3\}_6$	135°
$C_6\{O_2C(CH_2)_3CH_3\}_6$	109°
$C_6\{O_2C(CH_2)_5CH_3\}_6$	85.5°
$C_6\{O_2C(CH_2)_9CH_3\}_6$	89.5°

If we take the esters with the four valeric acids, the influence of the ramification is also distinctly shown.

$C_6\{O_2CC(CH_3)_3\}_6$	M.P. 316° (decomp.)
$C_6\{O_2CCH_2CH(CH_3)_2\}_6$	167.5°
$C_6(O_2CCHCH_3C_2H_5)_6$	115.5°
$C_6\{O_2C(CH_2)_3CH_3\}_6$	109°

Although a structural formula can only give an incomplete idea of the shape of a three-dimensional molecule, the contrast between the esters of n.valeroic acid and trimethylacetic acid, as shown by the figure, is striking enough, however.



Summarized, the chemical differences between both compounds are:

Low m.p., very good solubility in all organic solvents and easy formation for the former substance; high m.p., limited solubility only in high-boiling solvents and difficult formation for the latter.

Though the *amides of hexa-aminobenzene* decompose before or whilst melting, the rules generally hold good also here. So the valeric derivative with the longest side chain has the lowest decomposition point of all four isomeres. Amongst all amides prepared the lowest decomposition point is shown by the compound with the longest aliphatic side chain (heptanoic acid).

The *solubility* of the aliphatic esters of hexahydroxybenzene is fairly good; the longer the side chain is, the better the solubility. The acetate and trimethylacetate are very sparingly soluble, owing to the compact form of their molecules. The first substance is only slightly soluble in hot acetic acid, the second in hot high-boiling solvents. The aromatic esters are insoluble in the usual organic solvents and only sparingly soluble in boiling nitrobenzene, anisol, ethylbenzoate etc.

The derivatives of hexa-aminobenzene are practically insoluble in all organic solvents. Those with aliphatic acids may be recry-

stallized from the corresponding acids; on cooling the compounds often form gelatinous masses with the solvent. They are also soluble in cold concentrated sulfuric acid and are precipitated again if the solution is poured out into ice water. Besides they are soluble in hot alcohol containing 5 % sodium alcoholate. A marked exception is shown by the hexakistrimethylacetylaminobenzene, which is well soluble in benzene and similar solvents, but not in alcoholic alcoholate solution. This proves that the nitrogen atoms are made inaccessible by the encircling trimethylacetyl groups. From outward the substance resembles a hydrocarbon, which is in good agreement with its solubility in benzene.

The aromatic acyl derivatives do not dissolve either in alcoholic alcoholate solution, which is due to the same cause; the phenylacetyl compound on the other hand is fairly well soluble in it, and accordingly its decomposition point is lower than that of the trimethylacetyl and aromatic compounds.

The hexakis-p.chlorobenzoylaminobenzene does not dissolve in any solvent; it could only be purified by extracting the impurities with pyridine and butylphtalate.

As already mentioned, steric hindrance manifested itself in the synthesis of the trimethylacetyl compounds. In the case of hexahydroxybenzene a penta ester could be isolated; with hexa-aminobenzene it was impossible to get by means of the anhydride a product with more than approximately four acyl groups. For the hexa product the acid chloride and pyridine method proved to be successful. The same difficulties were met in the case of the methylethylacetyl compound.

The esters of hexahydroxybenzene crystallize well; they form thin, long needles in the case of esters of aliphatic acids with long straight side chains, and have a more compact model when the molecule, too, has a more compact shape. In the latter case the crystals form rhomboeders when the system is trigonal and prisms of pseudo hexagonal form when the system is monoclinic or triclinic. There may be a pretty great variation in the measurements of the angles of different crystals of one substance, even if this is repeatedly purified and the analysis shows correct figures.

The derivatives of hexa-aminobenzene crystallize in microscopical little needles, except the acetate and trimethylacetate, but the crystals of the acetate were too small for measurements.

Hexa-aminobenzene could be completely methylated with the aid of a large excess of dimethyl sulphate and potassium hydroxide. Hexakis-dimethylamino-benzene $C_6\{N(CH_3)_2\}_6$ melts at 236°. In contradistinction to hexa-aminobenzene it is very stable, insoluble in water, easily soluble in aromatic and aliphatic hydrocarbons, slightly so in alcohol and acetone. It forms with hydrochloric acid a trihydrochloride.

Several attempts to methylate hexahydroxybenzene failed, also some experiments to prepare hexamercaptobenzene.

In the course of this investigation 1,3,5-trichlorobenzene-2,4-disulphonic acid and the strychnine salt of chlorobenzene tetrasulphonic acid were obtained.